



Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at <http://about.jstor.org/participate-jstor/individuals/early-journal-content>.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

ARTICLE X.

On the decomposing power of Water at high temperatures, by Richard A. Tilghman.

Read August 20, 1847.

It has long been noticed, that partial decomposition is often effected in attempting to render anhydrous, by heat, certain salts which require a comparatively high temperature for the expulsion of their water of crystallization. This effect is not limited to those salts which are capable of decomposition by the action of heat alone, but extends to many which, when previously rendered anhydrous, are entirely unaffected by this agent. The chloride of magnesium offers a striking instance of such an action, being almost entirely reduced to magnesia, with escape of hydrochloric acid, when its solution is evaporated by a strong heat; the anhydrous chloride, when obtained by other processes, is, on the contrary, unaffected by the highest heat.

Even chloride of calcium, a salt of a much stronger radical base, has been observed to give off a portion of acid, when all its water of crystallization is driven off by a red heat. In these and many other instances, it seems evident that the escaping water of the salt is the actual decomposing agent, and that the intensity of its action depends solely upon the degree of heat which the salt can sustain before giving it off.

Contact of the salt and water, at high temperatures, appears to be the only requisite of decomposition. It was, therefore, thought probable, that by exposing the salt, even in its anhydrous state, to a high heat, and passing over it a current of aqueous vapour, raised to a similar temperature, not only might the above-mentioned salts be completely decomposed, but also that many others which have hitherto given no such signs of partial decomposition, might be acted upon in a similar manner.

On making the experiment, it was found, that not only the anhydrous chloride of calcium, but also the chlorides of strontium and barium could be rapidly decomposed by exposing them, at a high red heat, to a current of steam; hydrochloric acid was copiously evolved, and escaped along with the excess of steam, while the bases of the respective salts were left in a free state; the lime remaining anhydrous from the intensity of the heat employed, while the baryta and strontia combined with a portion of aqueous vapour, and were found in the state of hydrates.

In these haloid salts, it is to be observed, that the addition of the elements of water is absolutely essential to the decomposition; as neither the hydrogen which is contained in the acid, nor the oxygen in the base, existed in the anhydrous salt. The action is, therefore, the result of a double decomposition between the steam and the chloride, as well as of the affinity of the liberated acid and base for water.

The oxysalts, the sulphates of magnesia, lime, strontia, and baryta, unlike the haloid salts just mentioned, contain, even in the anhydrous state, all the elements generally considered necessary for the separate existence of the acid and bases of which they are composed. The application of the strongest heats to these salts causes, however, no liberation of their acid; but, as with the chlorides, this effect is immediately produced by the passage of a current of steam over them at a high temperature, the baryta and strontia being left in the state of hydrates, and the other bases anhydrous.

The intensity of the affinity between the acid and base of the respective salts, is curiously illustrated by the gradual increase of the heat necessary for their decomposition by the aqueous vapour.

Thus the sulphate of magnesia gives off its acid to the current of steam at a low red heat, and consequently a large portion of the acid may be condensed in an undecomposed state. The sulphate of lime requires a high red heat for its decomposition, and on this account the greater part of its acid is resolved into sulphurous acid and oxygen gas. The decomposition of the sulphates of strontia and baryta, requires progressively higher heats, which, in the case of the last salt, must be raised even to low whiteness.

The subphosphate of lime, as it contains an acid much less volatile than sulphuric, combined with an excess of a powerful base which adds to its stability, was selected as one of the most difficult tests of this decomposing power of aqueous vapour: by a full white heat, however, its phosphoric acid was slowly disengaged. This phosphoric acid gave a white precipitate with nitrate of silver, showing that its liberation and subsequent condensation in contact with a great excess of aqueous vapour, had not prevented that change which heat is known to produce upon this acid.

It might be expected from the decomposition of the salts of baryta, that the sulphates and muriates of potash and soda would undergo the same change with even greater facility. But it was found, by experiment, that although the decomposition of these last salts commenced with facility, when they were exposed to steam at a red heat, yet the proportion of alkali thus liberated never exceeded a very small per centage of the residual salt, however long the operation might be continued. Attributing this peculiarity to the volatile nature of the liberated hydrates of potash and soda at high temperatures, substances capable of forming non-volatile combinations with the alkalies were mixed with their salts, previously to subjecting them to the action of the steam; the acids were then found to be completely disengaged with facility. The fact that both lime and magnesia, substances capable of forming chemical combinations of but the most feeble character with potash and soda, were found to produce the above effect, was considered as confirming, in a great measure, the hypothesis that the volatility of their hydrates was the cause of the apparent difficulty of completely decomposing the salts of these alkalies.

The subphosphates and subsilicates of lime, baryta, and strontia, act in the same man-

ner as lime and magnesia, and in all these cases the chemical combination is so feeble that, when cold, the alkali is disengaged by the solvent powers of water alone.

Alumina, which possesses so much of the acid character with respect to the strong bases, is proportionably more efficient than any of the preceding substances in aiding the decomposition of the alkaline salts: it remains in combination with the alkali, when cold, as a soluble aluminate; but is easily precipitated from its solution by a current of carbonic acid gas.

The calcination of potash alum leaves a mixture of alumina and sulphate of potash, which Berthier has long since stated to be converted into aluminate of potash by the continued action of heat alone, the sulphuric acid being expelled from the potash by the superior affinity of the alumina at a high temperature. By several careful repetitions of his experiment, in which the accidental presence of aqueous vapours was entirely prevented, no decomposition of this kind could be effected, even at a white heat. But by the contact of aqueous vapour, produced by the combustion of the fuel or otherwise, even in small quantity, and at much lower temperatures, the decomposition is rapidly produced. It, therefore, seems probable that the accidental contact of aqueous vapour was the actual but unnoticed cause of the decomposition in Berthier's experiment.

The powerful action of aqueous vapour upon anhydrous alum at a high temperature, suggested the possibility that a similar action might take place upon its mineral representative, the double silicate of alumina and potash, or common felspar. It will be remembered that this salt, by the simple substitution of sulphuric for the silicic acid which it contains, would be converted into anhydrous alum. To the action of heat alone, felspar presents this difference from alum, that the silicate of alumina is as unaffected by it as the silicate of potash itself; so that to produce an effect upon felspar analogous to that upon alum, the silicic acid of both the silicate of alumina and of the silicate of potash would have to be removed. Silicic acid, in a *free* state, having been long known to be slightly volatile in aqueous vapour at high temperatures, it was thought that, in the present case, it might, like the other acids, be disengaged even from a state of chemical combination, by the same agents. Steam was, therefore, passed slowly, for some time, over small fragments of highly heated felspar. Beyond partial fusion, no other visible change than a considerable degree of vesicularity in the parts most exposed was produced. These fragments, being finely pulverized and boiled in water, the concentrated solution was strongly alkaline, and proved, by the usual tests, to consist of aluminate of potash.

After water ceases to extract aluminate of potash from the powdered mineral, dilute sulphuric acid will produce from the residue a small proportion of alum. The actual analogy between alum and felspar, substances so distinct in their origin and general properties, yet differing only in the nature of their respective acids, is rendered still more striking by both thus yielding the same product, when deprived of their acids by the same agent. It is worthy of remark, that, although the actual contact of the steam in this experiment is confined to the mere surface of the small fragments of felspar, yet the chemical decomposition produced by it is not confined to that surface, but spreads by a

“cementation action,” through their entire mass: pulverization is, therefore, required to obtain evidence of the internal change which has been produced.

All the experiments, so far made, would indicate that the following was the general rule applicable to all salts capable of sustaining heat alone without decomposition.

Whenever a salt, from its own elements alone, or by the addition of those of water, can produce a volatile acid and a fixed base, the evolution of this acid and the liberation of this base will be determined by passing a current of aqueous vapour over the salt raised to a high temperature. When either the acid or base to be liberated forms a combination with water which can resist decomposition by the heat employed, the tendency to form such hydrates adds much to the decomposing power of the aqueous vapour. Although potash and soda are not by themselves fixed bases at high temperatures, yet by the use of the substances before mentioned, they can form combinations which are fixed, and by this means their salts come under the above rule.

The actual number of salts which have as yet been subjected to this mode of decomposition, is not very large; yet, from their perfect analogy of composition with many others, there can be but little doubt of the general extension of the principle.

The chlorides of potassium, sodium, barium, strontium, and calcium, being all thus decomposed, the bromides, iodides, and fluorides of the same and all weaker bases, must probably act in the same manner. The fluoride of calcium has, in fact, been found to do so, by experiment, hydrofluoric acid being freely evolved. In the same manner, from the decomposition of the sulphates, may be inferred that of the seleniates; from the silicates that of the borates.

The applicability of this simple mode of decomposition to the explanation of a great variety of geological changes, is too evident to escape the attention of those conversant with that science. In a future paper I hope to be able to give a more complete account of some interesting facts which have been observed in connexion with this subject, and to verify, by experiment, many points which must at present be left to inference and conjecture. In fact, although the existence of this law of decomposition was ascertained in 1842, yet it has only been within a few months that I have been able to give much attention to its investigation, which must be my excuse for the imperfect and hurried manner in which it is now communicated.

London, August 3d, 1847.